EXAMPLE: Potassium tetrachloroplatinate(II): K_2PtCl_4

Space group: *P*4/*mmm* (No. 123)

Lattice parameters: $a = b = 7.023$ Å, $c = 4.1486$ Å

Atomic positions:

Pt	1*a*:	0,0,0
K	2*e*:	0,½,½
Cl	4*j*:	*x*,*x*,0 ; *x* = 0.23247

(a) Draw the unit cell with the atoms.

(b) Draw the projection of the unit cell in *c*-axis direction.

(c) Theoretical density is 3.37 g/cm^3. Calculate *Z*?
(N_A = 6.022 x 10^{23}; atomic weights: K 39.098; Pt 195.22; Cl 35.453)

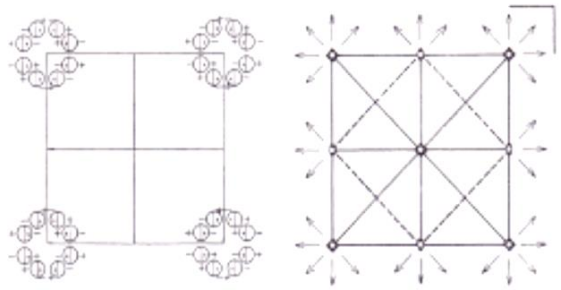
(d) Calculate the distances: Pt-Pt, Pt-K, Pt-Cl.

(e) What is the coordination number of platinum?

(f) What is the site symmetry of platinum?

$P\,4/m\,m\,m$ D^1_{4h} $4/m\,m\,m$ Tetragonal

No. 123 $P\,4/m\,2/m\,2/m$ Patterson symmetry $P\,4/m\,m\,m$



Origin at centre ($4/m\,m\,m$)

Asymmetric unit $0\le x\le\frac{1}{4};\ 0\le y\le\frac{1}{4};\ 0\le z\le\frac{1}{4};\ x\le y$

Symmetry operations

(1) 1 (2) 2 0,0,z (3) 4^+ 0,0,z (4) 4^- 0,0,z
(5) $\bar{2}$ 0,y,0 (6) 2 x,0,0 (7) $\bar{2}$ x,x,0 (8) $\bar{2}$ x,$\bar{x}$,0
(9) $\bar{1}$ 0,0,0 (10) m x,y,0 (11) $\bar{4}^+$ 0,0,z; 0,0,0 (12) $\bar{4}^-$ 0,0,z; 0,0,0
(13) m x,0,z (14) m 0,y,z (15) m x,$\bar{x}$,z (16) m x,x,z

Pt	1*a*:	0,0,0
K	2*e*:	0,½,½
Cl	4*j*:	x,x,0 ; x = 0.23247

Maximal non-isomorphic subgroups

I [2]$P\,4\,2\,2$ 1; 2; 3; 4; 5; 6; 7; 8
[2]$P\,4/m\,1\,1$ ($P\,4/m$) 1; 2; 3; 4; 9; 10; 11; 12
[2]$P\,4\,m\,m$ 1; 2; 3; 4; 13; 14; 15; 16
[2]$P\,\bar{4}\,2\,m$ 1; 2; 5; 6; 11; 12; 15; 16
[2]$P\,\bar{4}\,m\,2$ 1; 2; 7; 8; 11; 12; 13; 14
[2]$P\,2/m\,2/m\,1$ ($P\,m\,m\,m$) 1; 2; 5; 6; 9; 10; 13; 14
[2]$P\,2/m\,1\,2/m$ ($C\,m\,m\,m$) 1; 2; 7; 8; 9; 10; 15; 16

IIa none

IIb [2]$P\,4/m\,c\,c$ ($c'=2c$); [2]$P\,4_2/m\,m\,c$ ($c'=2c$); [2]$P\,4_2/m\,c\,m$ ($c'=2c$); [2]$C\,4/a\,m\,d$ ($a'=2a, b'=2b$) ($P\,4/n\,b\,m$);
[2]$C\,4/m\,m\,d$ ($a'=2a, b'=2b$) ($P\,4/m\,b\,m$); [2]$C\,4/a\,m\,m$ ($a'=2a, b'=2b$) ($P\,4/n\,m\,m$);
[2]$F\,4/m\,m\,m$ ($a'=2a, b'=2b, c'=2c$) ($I\,4/m\,m\,m$); [2]$F\,4/m\,m\,c$ ($a'=2a, b'=2b, c'=2c$) ($I\,4/m\,c\,m$)

Maximal isomorphic subgroups of lowest index

IIc [2]$P\,4/m\,m\,m$ ($c'=2c$); [2]$C\,4/m\,m\,m$ ($a'=2a, b'=2b$) ($P\,4/m\,m\,m$)

Minimal non-isomorphic supergroups

I [3]$P\,m\,\bar{3}\,m$

II [2]$I\,4/m\,m\,m$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3); (5); (9)

Positions

Multiplicity, Wyckoff letter, Site symmetry		Coordinates				Reflection conditions
16	u	1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $\bar{y},x,z$	(4) $y,\bar{x},z$
			(5) $\bar{x},y,\bar{z}$	(6) $x,\bar{y},\bar{z}$	(7) $y,x,\bar{z}$	(8) $\bar{y},\bar{x},\bar{z}$
			(9) $\bar{x},\bar{y},\bar{z}$	(10) $x,y,\bar{z}$	(11) $\bar{y},x,\bar{z}$	(12) $y,\bar{x},\bar{z}$
			(13) $x,\bar{y},z$	(14) $\bar{x},y,z$	(15) $y,\bar{x},z$	(16) $\bar{y},x,z$
						General: no conditions
						Special:
8	t	$.m.$	$x,\frac{1}{2},z$ $\bar{x},\frac{1}{2},\bar{z}$	$\bar{x},\frac{1}{2},z$ $x,\frac{1}{2},\bar{z}$	$\frac{1}{2},x,z$ $\frac{1}{2},\bar{x},\bar{z}$	$\frac{1}{2},\bar{x},z$ $\frac{1}{2},x,\bar{z}$	no extra conditions
8	s	$.m.$	$x,0,z$ $\bar{x},0,\bar{z}$	$\bar{x},0,z$ $x,0,\bar{z}$	$0,x,z$ $0,\bar{x},\bar{z}$	$0,\bar{x},z$ $0,x,\bar{z}$	no extra conditions
8	r	$..m$	x,x,z $\bar{x},\bar{x},\bar{z}$	$\bar{x},\bar{x},z$ $x,x,\bar{z}$	$\bar{x},x,z$ $x,\bar{x},\bar{z}$	$x,\bar{x},z$ $\bar{x},x,\bar{z}$	no extra conditions
8	q	$m..$	$x,y,\frac{1}{2}$ $\bar{x},\bar{y},\frac{1}{2}$	$\bar{x},\bar{y},\frac{1}{2}$ $x,y,\frac{1}{2}$	$\bar{y},x,\frac{1}{2}$ $y,\bar{x},\frac{1}{2}$	$y,\bar{x},\frac{1}{2}$ $\bar{y},x,\frac{1}{2}$	no extra conditions
8	p	$m..$	$x,y,0$ $\bar{x},\bar{y},0$	$\bar{x},\bar{y},0$ $x,y,0$	$\bar{y},x,0$ $y,\bar{x},0$	$y,\bar{x},0$ $\bar{y},x,0$	no extra conditions
4	o	$m\,2m$	$x,\frac{1}{2},\frac{1}{2}$	$\bar{x},\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},x,\frac{1}{2}$	$\frac{1}{2},\bar{x},\frac{1}{2}$	no extra conditions
4	n	$m\,2m$	$x,\frac{1}{2},0$	$\bar{x},\frac{1}{2},0$	$\frac{1}{2},x,0$	$\frac{1}{2},\bar{x},0$	no extra conditions
4	m	$m\,2m$	$x,0,\frac{1}{2}$	$\bar{x},0,\frac{1}{2}$	$0,x,\frac{1}{2}$	$0,\bar{x},\frac{1}{2}$	no extra conditions
4	l	$m\,2m$	$x,0,0$	$\bar{x},0,0$	$0,x,0$	$0,\bar{x},0$	no extra conditions
4	k	$m\,.\,2m$	$x,x,\frac{1}{2}$	$\bar{x},\bar{x},\frac{1}{2}$	$\bar{x},x,\frac{1}{2}$	$x,\bar{x},\frac{1}{2}$	no extra conditions
4	j	$m\,.\,2m$	$x,x,0$	$\bar{x},\bar{x},0$	$\bar{x},x,0$	$x,\bar{x},0$	no extra conditions
4	i	$2m\,m\,.$	$0,\frac{1}{2},z$	$\frac{1}{2},0,z$	$0,\frac{1}{2},\bar{z}$	$\frac{1}{2},0,\bar{z}$	hkl : $h+k=2n$
2	h	$4m\,m$	$\frac{1}{2},\frac{1}{2},z$	$\frac{1}{2},\frac{1}{2},\bar{z}$			no extra conditions
2	g	$4m\,m$	$0,0,z$	$0,0,\bar{z}$			no extra conditions
2	f	$m\,m\,m$	$0,\frac{1}{2},0$	$\frac{1}{2},0,0$			hkl : $h+k=2n$
2	e	$m\,m\,m$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,\frac{1}{2}$			hkl : $h+k=2n$
1	d	$4/m\,m\,m$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$				no extra conditions
1	c	$4/m\,m\,m$	$\frac{1}{2},\frac{1}{2},0$				no extra conditions
1	b	$4/m\,m\,m$	$0,0,\frac{1}{2}$				no extra conditions
1	a	$4/m\,m\,m$	$0,0,0$				no extra conditions

Symmetry of special projections

Along [001] $p\,4m\,m$ $a'=a$ $b'=b$ Origin at $0,0,z$

Along [100] $p\,2m\,m$ $a'=b$ $b'=c$ Origin at $x,0,0$

Along [110] $p\,2m\,m$ $a'=\frac{1}{2}(-a+b)$ $b'=c$ Origin at $x,x,0$

(*Continued on preceding page*)

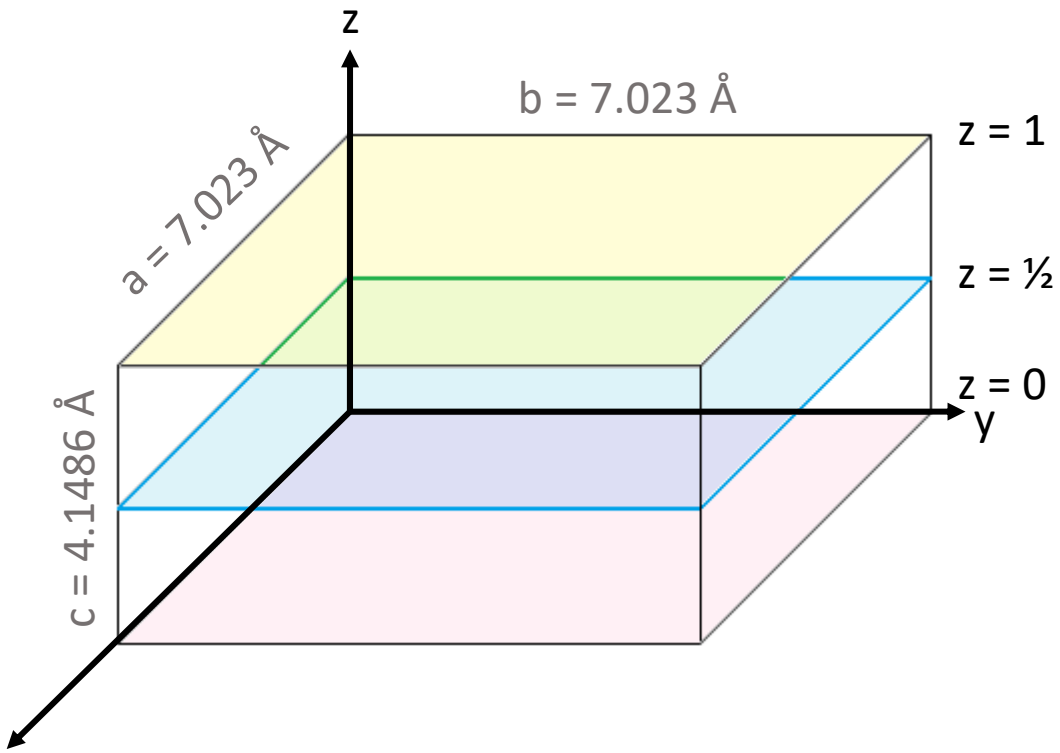
List all atom duplicates based on Wyckoff position

Atom	*Wyckoff site*	*Atom counting*	*Position*	*Coordinates*
Pt	1 a	1	0 0 0	0 0 0
K	**2 e**	**1**	**0, ½, ½**	**0, ½, ½**
		2	**½, 0, ½**	**½, 0, ½**
Cl	**4 j**	**1**	**x, x, 0 (x=0.23247)**	**0.23, 0.23, 0**
		2	**-x, -x, 0**	**0.77, 0.77, 0**
		3	**-x, x, 0**	**0.77, 0.23, 0**
		4	**x, -x, 0**	**0.23, 0.77, 0**

Drawing tactic: framework

a = *b* = 7.023 Å, *c* = 4.1486 Å

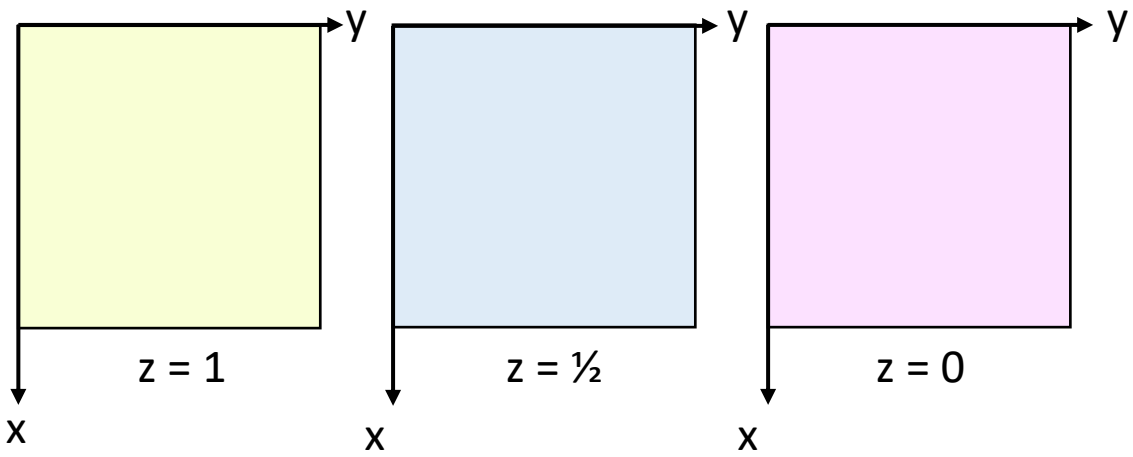
→ The box is a bit flat, more wide than high



Atoms have z coordinates 0 and ½

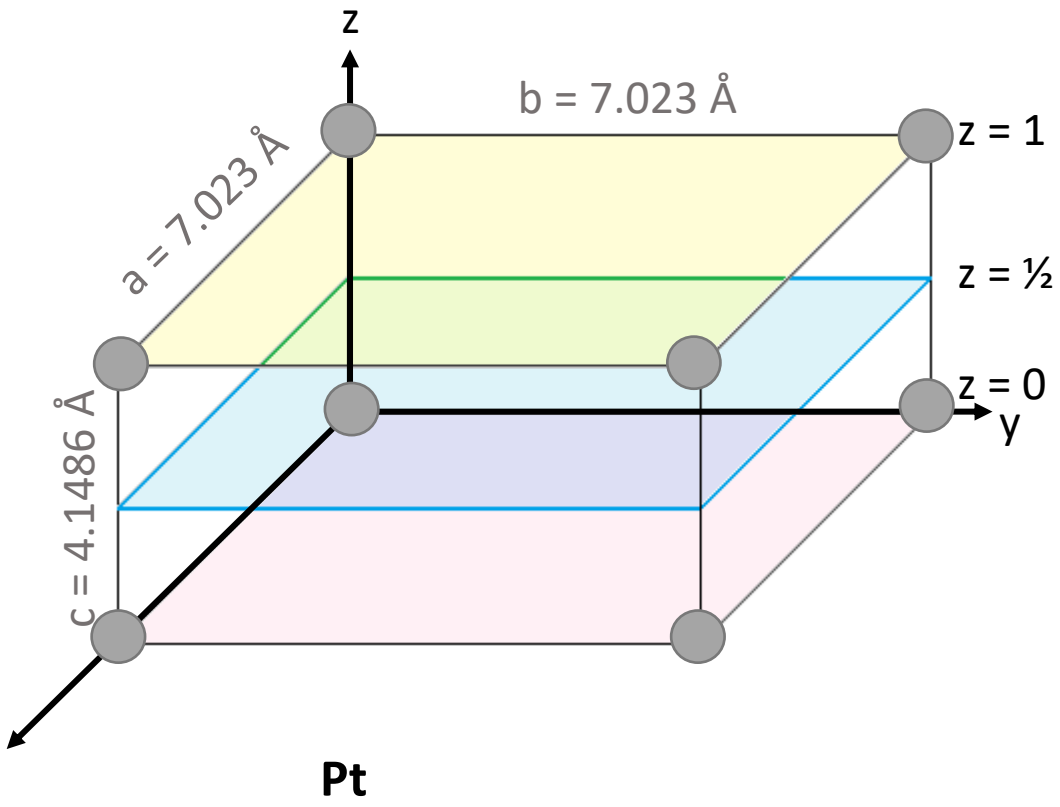
→Three 'levels' in the structure

(since z=0 means we also draw those atoms at z=1)

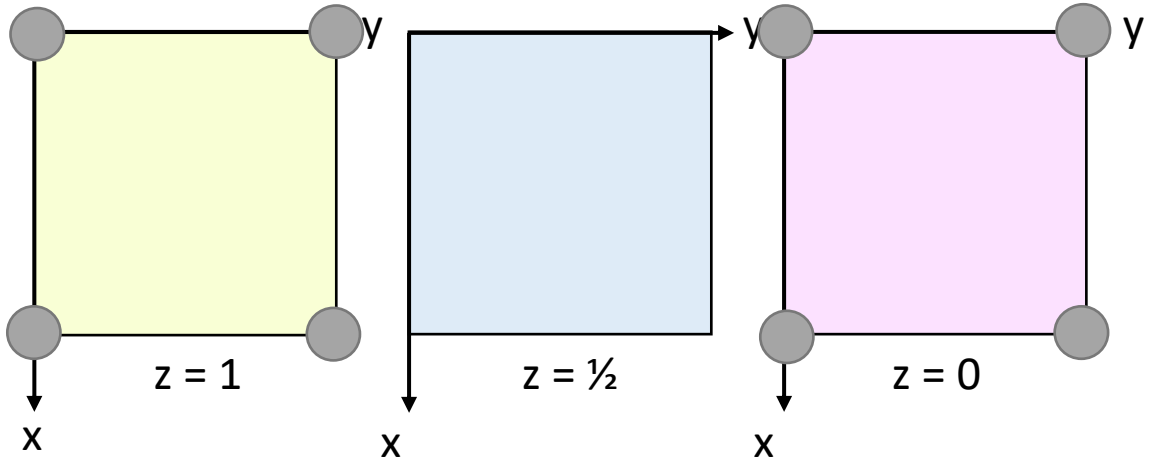


Drawing tactic: add atom Pt

Atom Pt is at (0, 0, 0) = in each cormer

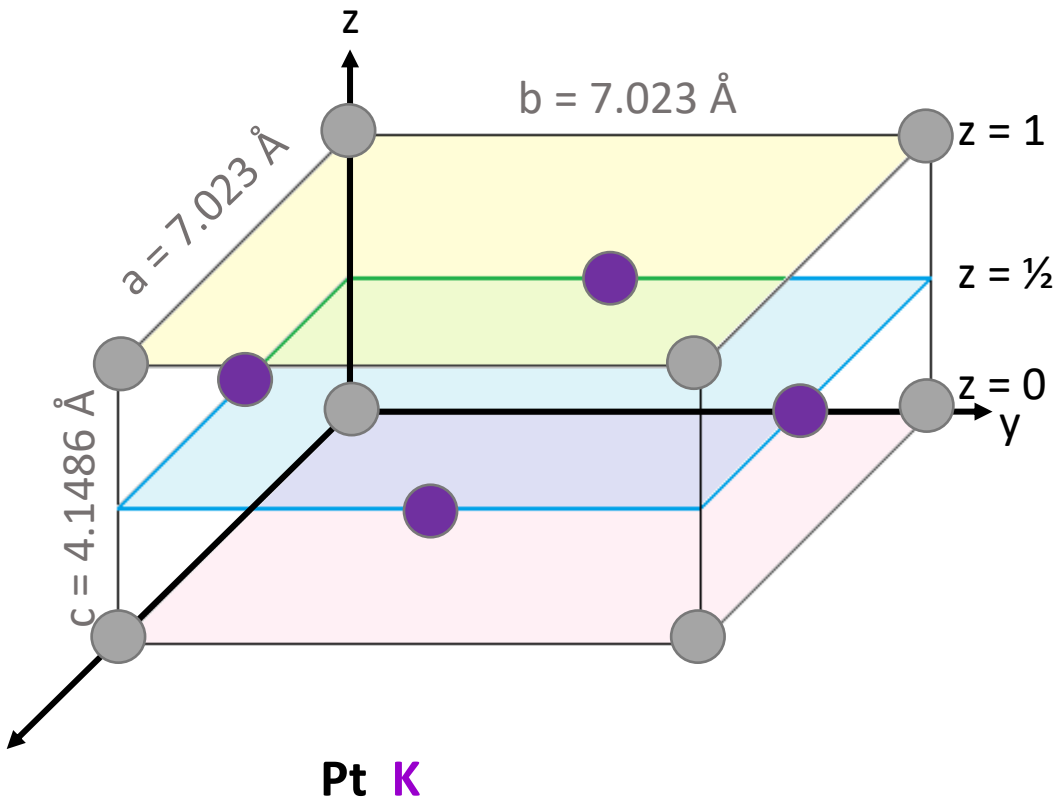


Also add these same atoms in the 'floor plan' drawings for z=0 and z=1

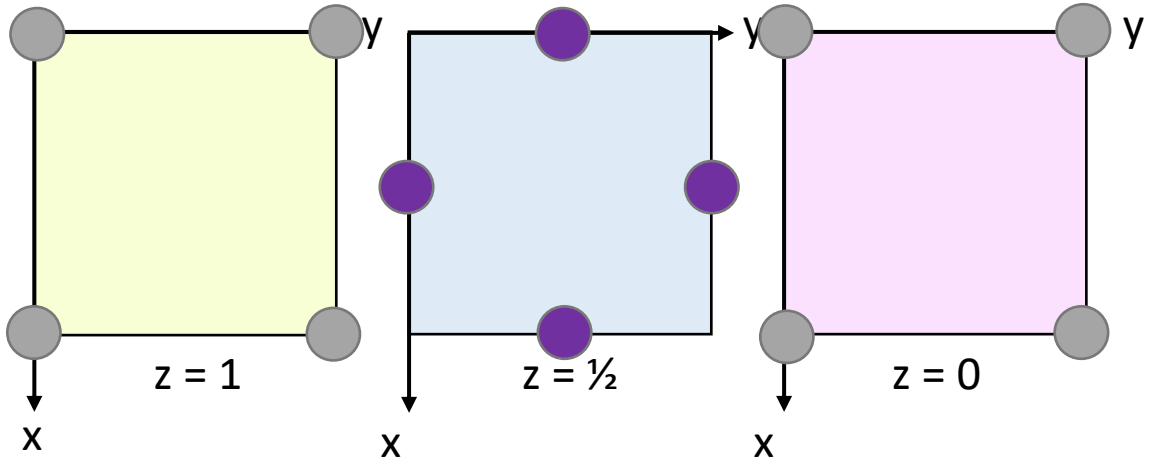


Drawing tactic: add atom K

Atom K is at (0, ½, ½) & (½, 0, ½)
= middle of each side face (”outer walls”)



Add these in the ’floor plan’ drawings,
all of them are on level z=½



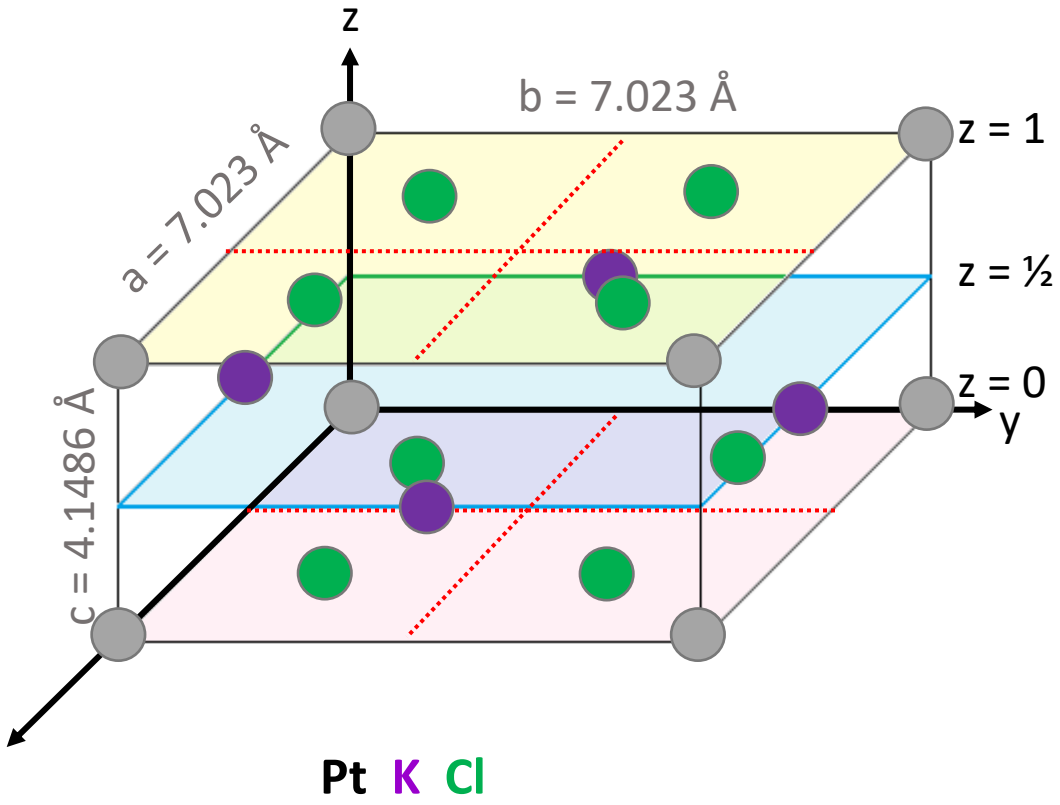
Drawing tactic: add atom Cl

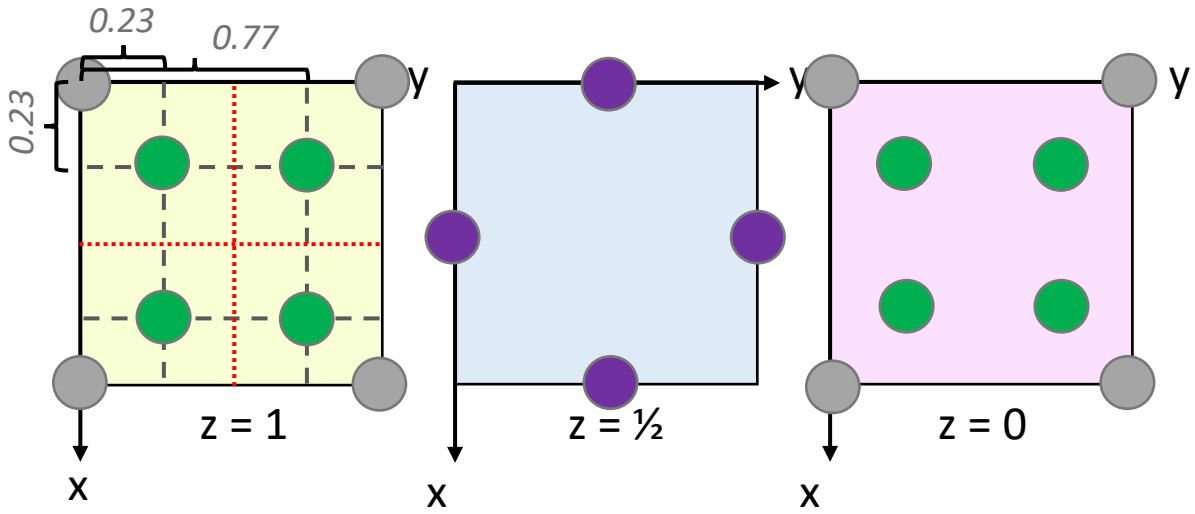
- Atom K has four positions: (0.23, 0.23, 0); (0.77, 0.77, 0); (0.77, 0.23, 0); and (0.23, 0.77, 0)

All of these atoms are on the z=0 and z=1 drawings only.

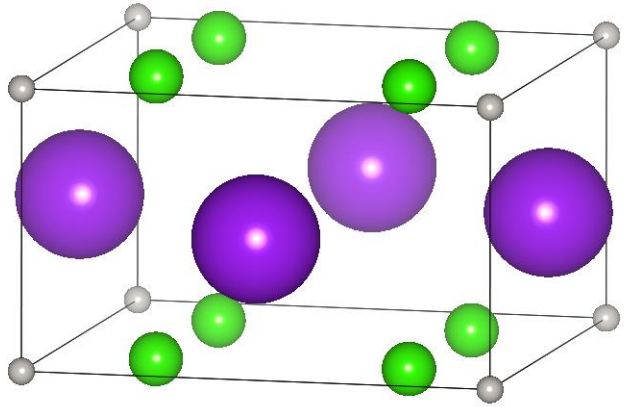
In this case it might be easier to find their locations here first, and then copy to the box drawing.

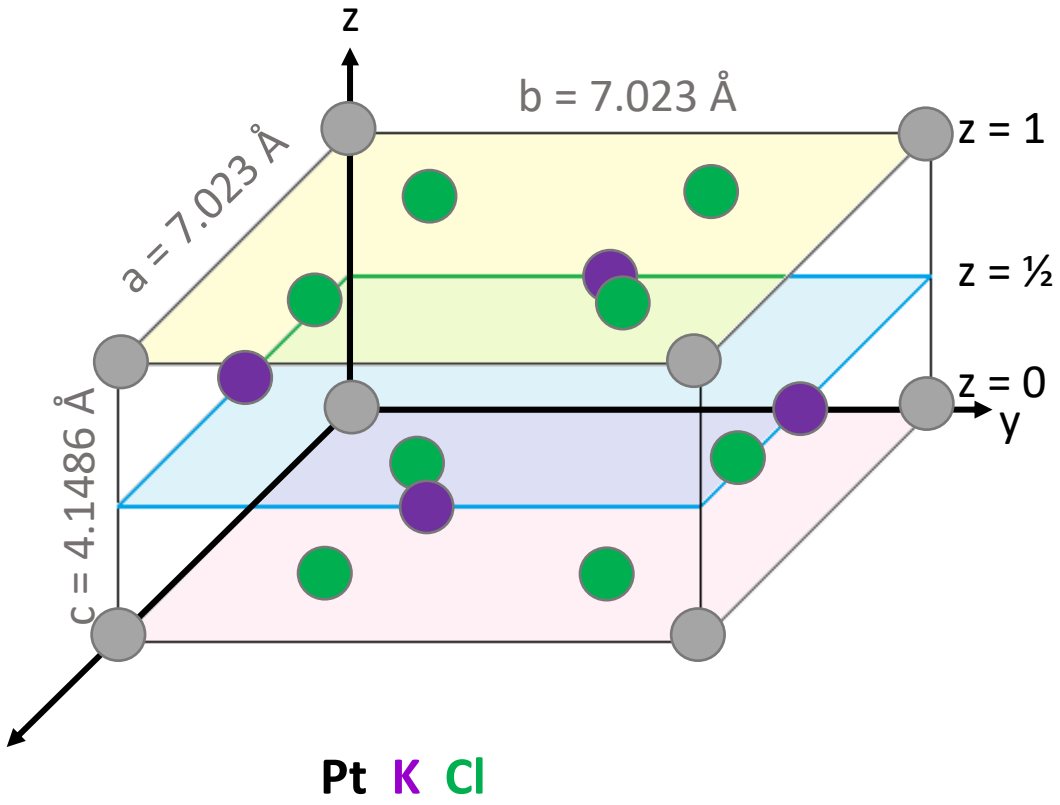
The approximate location is in the middle of the 'quarters' of level z=0 and z=1

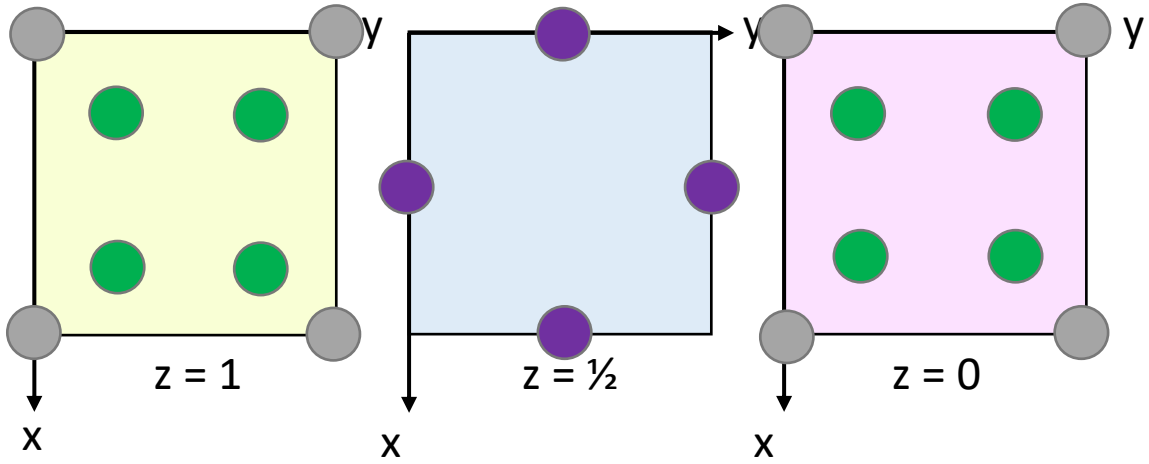




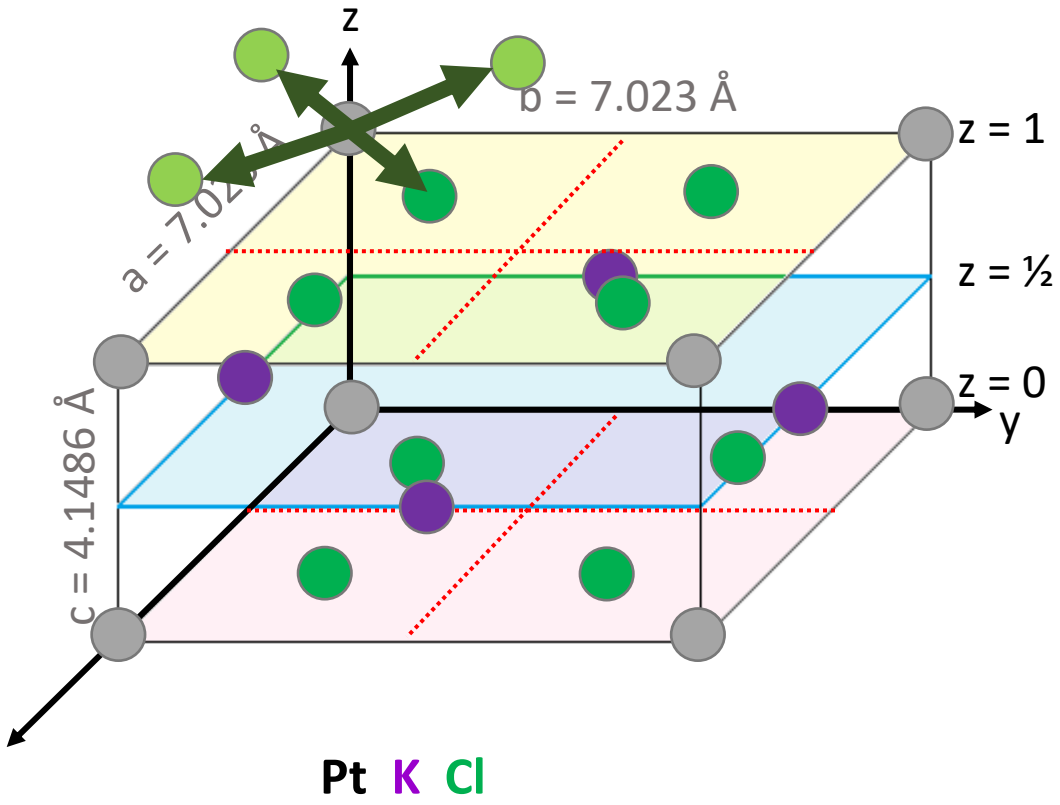
Compare to the image made in Vesta





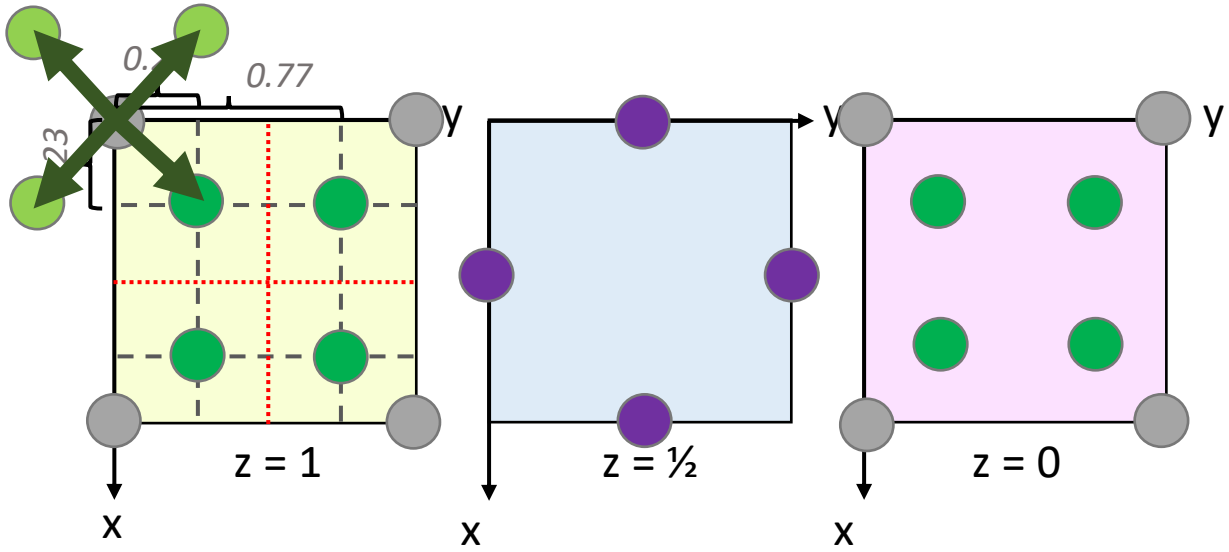


Nearby atoms and bond distances



The floor drawings show the nearby atoms in the same plane:

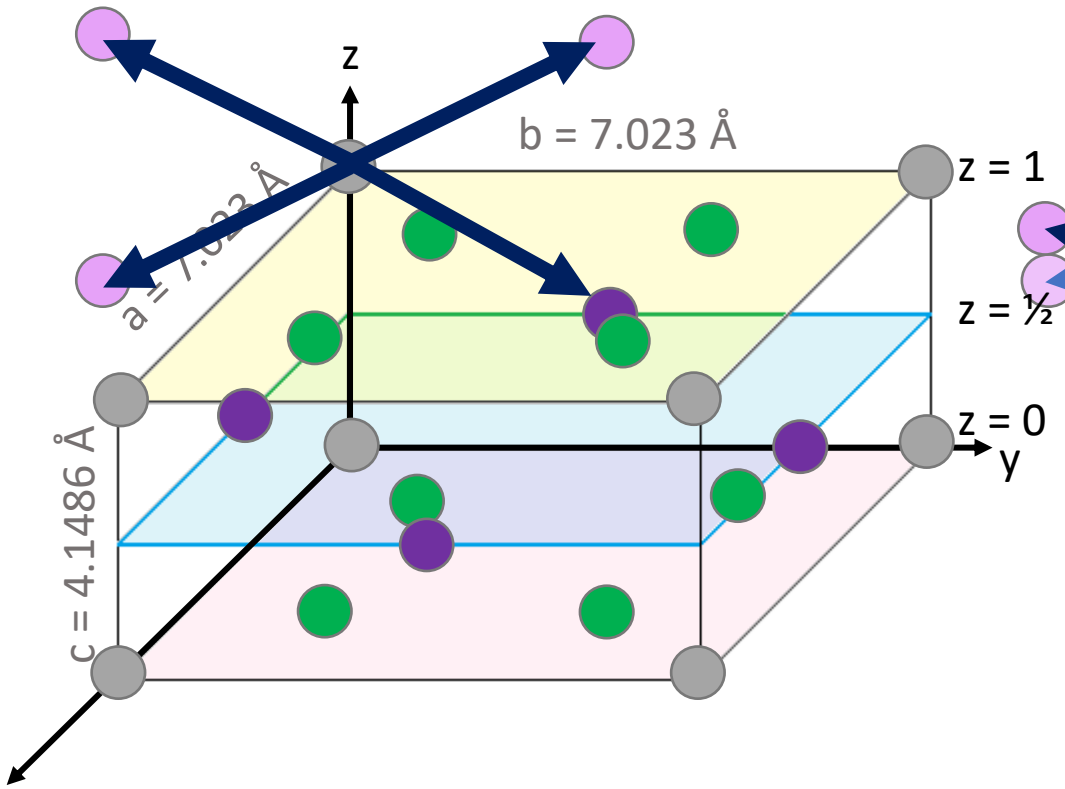
Pt has neighbour Cl-atoms in diagonal directions (remember the neighbor cells also)



Pt-Cl bond length can be found by trigonometry:

$$L = \sqrt{(x_{Pt} - x_{Cl})^2 + (y_{Pt} - y_{Cl})^2 + (z_{Pt} - z_{Cl})^2}$$

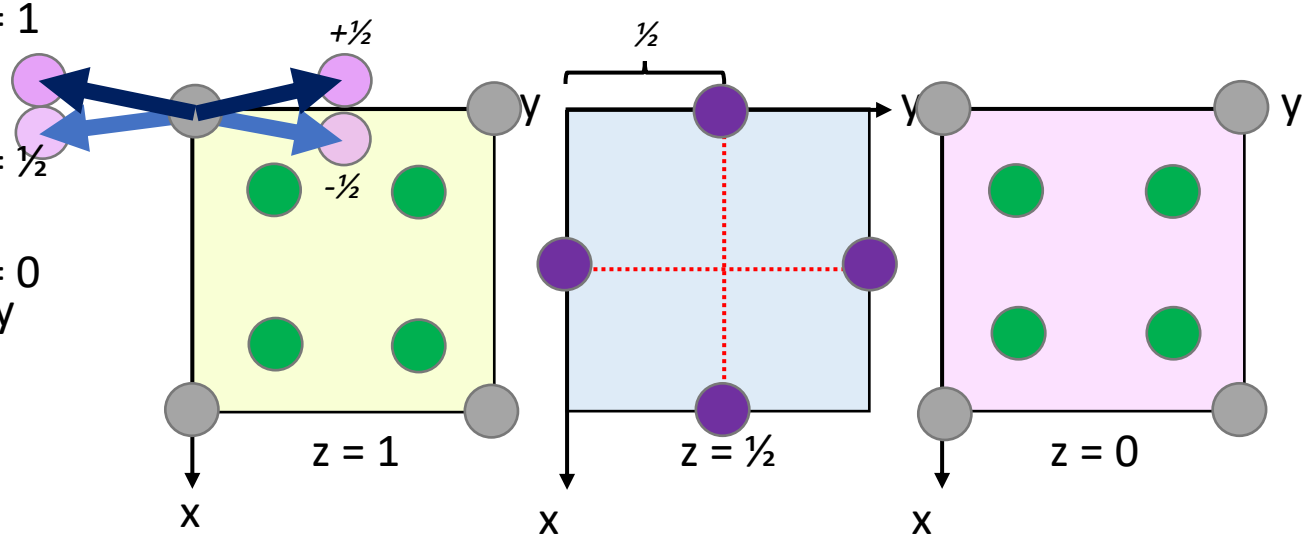
Nearby atoms and bond distances



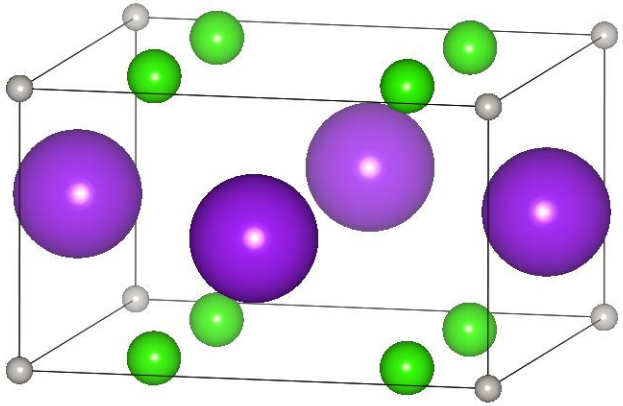
Pt **K** **Cl**

The box drawing helps see atoms that are neighbouring in different planes

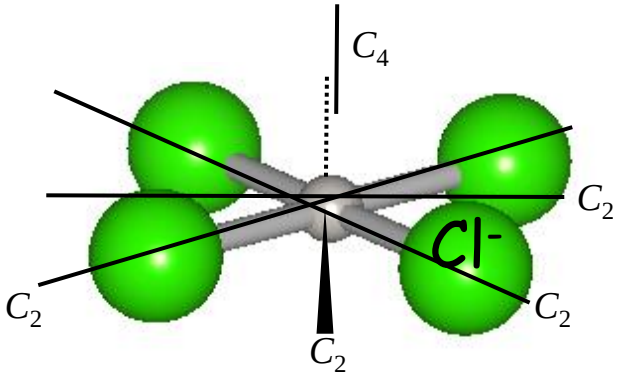
Pt has neighbour K-atoms diagonally up the ”walls”; the atom coordinates can also be read from the floor drawings



$$L = \sqrt{(x_1 - x_1)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}$$

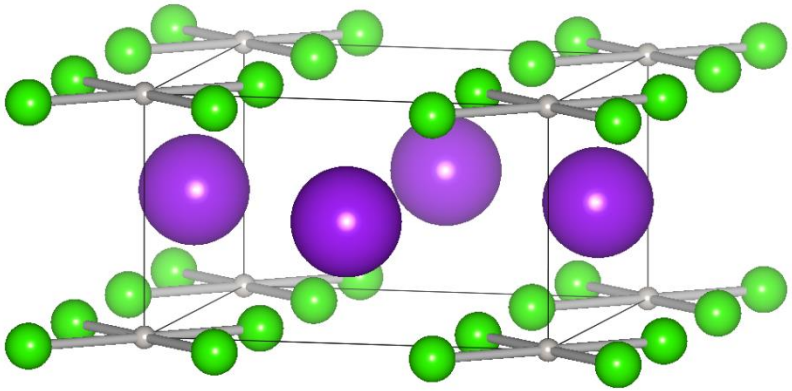


Pt: 1 atom in unit cell
K: 2 atoms in unit cell
Cl: 4 atoms in unit cell

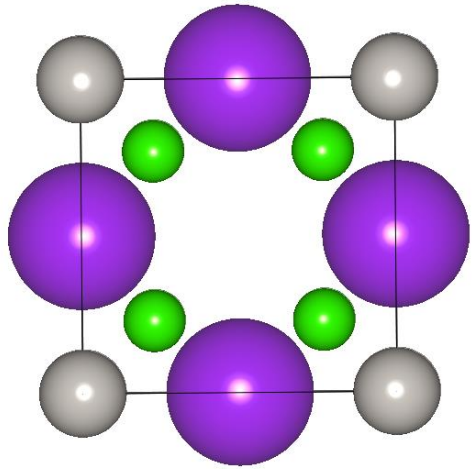


Site symmetry of Pt: D_{4h}

Bond lengths:
Pt-Pt: $(1-0)^2 \cdot 4.15Å$
Pt-K: $\sqrt{[(0.5-0)^2 \cdot 7.023Å + (0.5-0)^2 \cdot 4.149Å]} = 4.08Å$
Pt-Cl: $\sqrt{[(0.232-0)^2 \cdot 7.023Å + (0.232-0)^2 \cdot 7.023Å]} = 2.30Å$



ab-projection
(seen from *c*-direction)



K_2PtCl_4

- $\rho = 3.37 \times 10^6$ g/m^3
- V = 7.023 Å x 7.023 Å x 4.1486 Å = 204.62×10^{-30} m^3
- M = (2 x 39.098 + 195.22 + 4 x 35.453) g/mol = 415.228 g/mol
- $Z = (V \times \rho \times N_A) / M = 1$
- Distances: Pt-Pt: 4.15 Å
  Pt-K: 4.08 Å
  Pt-Cl: 2.31 Å ($\rightarrow$ chemical bond)

Too long distance → not a chemical bond, but can have electrostatic attraction

- CN(Pt) = 4
- Pl site symmetry: D_{4h}